THESIS

FACTORS GOVERNING THE NITRATION OF CELLULOSE

W. B. Robertson 1946 Linear I

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A Thesis

Presented to the Faculty of the Graduate School of Cornell
University for the degree of
Master of Science

Wilson Pee Robertson
June, 1946

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The author was born at Anding, Lississippi, on March 17, 1918, the son of Janie See and Joseph Barnes Robertson. He received his early education in the public schools of New Orleans, Louisiana, and wessen, Elssissippi.

After completing one year at Copish-Lincoln Junior College, Messon, Mississippi, he attended Louisiana State University, where he rajored in Chemical Engineering. He was graquated in May, 1939, with the degree of Eachelor of Science.

Upon graduation, he was employed in the engineering division of Few Orleans Fublic Service, Inc., and later, in the Flood Control Laboratory, U.S. Engineers, Tew Orleans, Louisians.

he received a commission in the United States Laval Reserve in October, 1941, and served successively in the Ordnance Section, Favy Yard, New York, and aboard the U.S.S. Ballard.

In Feverber, 1945, he enrolled in the graduate school of Cornell University to commence a course in explosives, majoring in Chemical Engineering.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor F. A. Rhodes and to the other members of the faculty of the Department of Chemical Engineering and the Department of Chemistry of Cornell University who have contributed to his education and training.

The author is greatly indebted to his wife, hazel S. Robertson, for her help in producing this thesis.

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INTRODUCTION.

Cellulose was probably first nitrated, in 1636, by Theophile-Jules Pelouze. 32 who prepared nitrocellulose by dipping paper into concentrated nitric acid. Sarlier, in 1833, H. Iraconnot 32 had prepared a nitric ester of starch by dissolving starch in concentrated nitric acid and then diluting it with water to precipitate the eater, which he called "xyloidine". The products that Felcuse obtained from paper, cotton and linen were considered to be identical with the xyloidine from starch. 1846 Pelcuse32 made clear distinction between xyloidine and the cellulose ester, which he called "pyroxyline". In 1645, Christian Friedrich Schonbien at Basal, Germany, used a mixture of mitric acid and sulfuric acid to mitrate cotton. Later that same year Rudolf bottger, e professor at Frankfort-on-the-bain, independently prepared guncotton. Schonbien's process, in which he used a ratio of one volume of strong nitric acid (density 1.45 to 1.5) to three volumes of strong sulfuric acid (density 1.85), became the basis for the commercial manufacture of guncotton for explosives.

It is possible to propare cellulose nitrate of various degrees of substitution depending upon the conditions of nitration. The completely substituted product is cellulose trinitrate, which has a nitrogen content of 14.14 per cent. The theoretical equation for the reaction is:

 $C_6H_7O_2(OH)_3 + 3HO_3 = C_6H_7O_2(ONO_2)_3 + 3H_2O$ Technically, the reaction is an esterification rather than a

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 nitration, but the latter term is more commonly used.

Although nitrocellulose was initially used only as a military explosive, products of lower nitration have since become extremely important in the plastics and lacquer industries. The applications of the various classes of nitrocelluloses and their corresponding nitrogen contents are: 25

Fer Cent	Field of Application			
10.7 - 11.2	Celluloid plastics, leoquers			
11.2 - 11.7	Film, lacquers			
11.8 - 12.3	Film, locquers, rayon, coated			
	fabrics, cements			
12.5 - 13.5	Smokeless powder			

It is the purpose of this paper to consider the various factors which control the degree of nitration of cellulose when mixed acid is used as the nitrating agent.

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The chemical substitution which takes place when cellulose is nitrated with mixed acid is effected with little alteration in the physical appearance or fiber structure of the cellulose. The fibers appear merely to become somewhat harder and more brittle; with cotton, the convoluted fibers become untwisted.

Although the precise manner in which the substitution takes place in cellulose fibers is not known, two general concepts have been proposed to explain the reaction. According to the first of these concepts, the cellulose micelles are penetrated by the nitration reagent and the reaction proceeds progressively from the exterior to the interior of the micelles in a heterogeneous fashion. In other words, the molecules encountered first are nitrated completely to the trinitrate, while other and more inaccessible molecules remain unchanged. The supporters of this theory contend that cellulose nitrate containing less nitrogen than the trinitrate is a mixture of cellulose trinitrate and unchanged cellulose. The second, and more generally accepted concept proposes that the nitration reagent penetrates uniformly into all parts of the cellulose fiber and that the entire fiber is nitrated homogeneously at approximately the same time.

X-Ray examinations of cellulose of various degrees of substitution have provided some clue as to the structure of cellulose nitrate and the nature of the nitration reaction, although the interpretations of the X-ray patterns and the conclusions arrived at by various investigators are not in agreement. and the state of the contract of the state of the contract of

-COR 10 described could be 25 market by the combined work of the combined work of the country of

R. O. Merzeg, S. von Narey-Szabo, and G. von cusion 13,23 concluded, after examining the structure of different specimen of nitro-cellulose, that all nitrocelluloses below the trinitrate are mixtures of cellulose trinitrate and unchanged cellulose. Among others who have investigated the X-ray patterns of nitrocelluloses of various compositions are F. D. Niles and J. Craik²¹.

M. A. Sissen²⁹, M. Mathieu²⁰, and E. J. Lorand¹⁷.

F. D. Niles and J. Craik 21 observed that the K-ray pattern of cellulese does not change until a nitregen content of 7.6 per cent has been reached. At this point the crystalline pattern disappears, and an amorphous pattern persists until a nitrogen content of 10.3 per cent is reached. A crystalline pattern approaching that of cellulose trinitrate is not observed until the mitrogen content reaches 12.5 per cent. Mark 19 and Miles, Craik and Melbourn 21,22 attribute the appearance of the amorphous diagrem to a non-uniform distribution of ester groups, which prevents the development of a crystalline lattice structure. Miles and Craik21 state that in the first stage of nitration, up to about 7.5 per cent mitrogen content, only the diffractions of almost completely mercerized cellulose are observed, and suggest that substitution has taken place only on the "inner surface" of the fibers, while the interior of the micelles remain unaffected. They expressed the belief that, as nitration proceeds beyond the initial stage, the micellar arrangement breaks down and the nitrate groups become so distributed among the chain molecules that there is little likelihood that any one molecule becomes completely nitrated to the

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trinitrate while others remain unchanged.

Heas and Trogus 15, who have been the chief supporters of the heterogeneous micellar theory, claim that the amorphous diagram is the result of the conversion of cellulose into its hydrate form which takes place under the swelling influence of the strong acid. They contend that the amorphous diagram represents a mixture of unsubstituted cellulose with the trinitrates of both cellulose and cellulose hydrates.

According to the explanation advanced by A. A. Sisson²⁹, the reagent penetrates the fiber, attacking first the surface of the micelle, which is changed into the tri-derivative; then proceeds inward to produce, between the unreacted interior and the completely reacted surface, a partially reacted area in which only two hydroxyl groups have been replaced by nitrate groups. This partially reacted area is responsible for the amorphous X-ray diagram produced.

E. J. Lorand 17 states that there is evidence to support the view that all cellulose nitrations do not follow a single pattern, and that the type of reaction depends upon the nature of the nitration reagents used and their concentrations, the temperature, and other conditions. It is probable, according to Lorand, that the permutoid or quasi-homogeneous, the micellar heterogeneous, and other types of proposed reactions may apply, depending upon the circumstances.

The failure to find any appreciable amount of unchanged cellulose or any evidence of the presence of completely substituted

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cellulose trinitrate²¹ in nitrocellulose samples has resulted in considerable opposition to the micellar heterogeneous theory.

**Lumerous samples of nitrocellulose have been fractionated; none of the fractions have varied more than 0.3 per cent in nitrogen content.

Additional evidence, based upon measurements of menomolecular films of nitrocellulose spread on a two-normal sodium hydroxide solution has been introduced by F. D. biles to discredit the micellar heterogeneous theory. Miles contends that in order for the nitrocellulose structure to exist, as supposed by mess and Trogus, either the micelle must solvate or disperse as such, in which case he claims that it is impossible to account for the spreading of the single molecule; or, the cellulose trinitrate must separate from the unchanged cellulose. If the latter were true, tiles points out, only the cellulose trinitrate would spread and the resulting film area would be less than that actually found.

Lany investigators 21,22,25 have produced evidence that cellulose nitration is a reversible reaction and involves the usual principles of esterification. That is, when molecular quantities of nitric acid and cellulose react, an ester is formed and water is split out. Since the reverse reaction takes place at the same time, an equilibrium is set up between the cellulose, acid, water and ester. The reaction approaches completion when an excess of the nitric acid is taken and sulfuric acid is used to combine with the water formed. The existence of equilibria has been observed over a wide range of substitution, and it has been shown 25

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that the final nitregen content of the product is determined by the final composition of the nitrating bath.

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Tota INFLUSACE OF WATER IN THE MITHATION ACID

The proportion of water present in the mixed acid used for nitration is directly related to the degree of substitution of the resulting product. The effect of the variation of the water content of the nitrating mixture upon the nitrogen content of the nitrocellulose prepared was first investigated systematically by hunge and Bebie¹⁸. By maintaining the ratio of sulfuric acid to nitric acid constant, they nitrated medical cotton with acid mixtures of increasing water content. Equal weights of nitric acid (94.09 per cent) and sulfuric acid (92.10 per cent) were used. The temperature during the reaction was kept at 16° to 18°C., and the duration of the reaction was twenty-four hours in each case.

Effect of mater Content of Mixed Acid on the Degree of Mitration of Cellulose 18

Ro.	Composi H ₂ SO ₄ , Fer Cent	tion of Mi HNO3. Per Cent	H ₂ O, Per Cent	Nitrogen in Nitrocellulose, Per Cent	Yield, Fer Cent
1	45.31	49.07	5.62	13.65	177.5
2	42.61	40.01	11.30	13.21	176.2
3	41.03	44.45	14.52	12.76	-
4	40.66	43.88	15.49	12.58	167.0
5	40.14	43.25	16.61	12.31	189.0
8	39.45	42.73	17.82	12.05	153.0
7	38.95	42.15	18.90	11.59	156.5
8	38.43	41.31	20.26	10.93	144.2
9	37.20	40.30	22.50	9.76	146.0
10	36.72	39.78	23.50	9.31	138.9
11	35.87	38.83	25.30	8.40	131.2
12	34.41	37.17	28.42	6.50	400

by plotting the amount of water added against the percentage of nitrogen in the product, the effect of increasing the water

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The Effect of the Water Content
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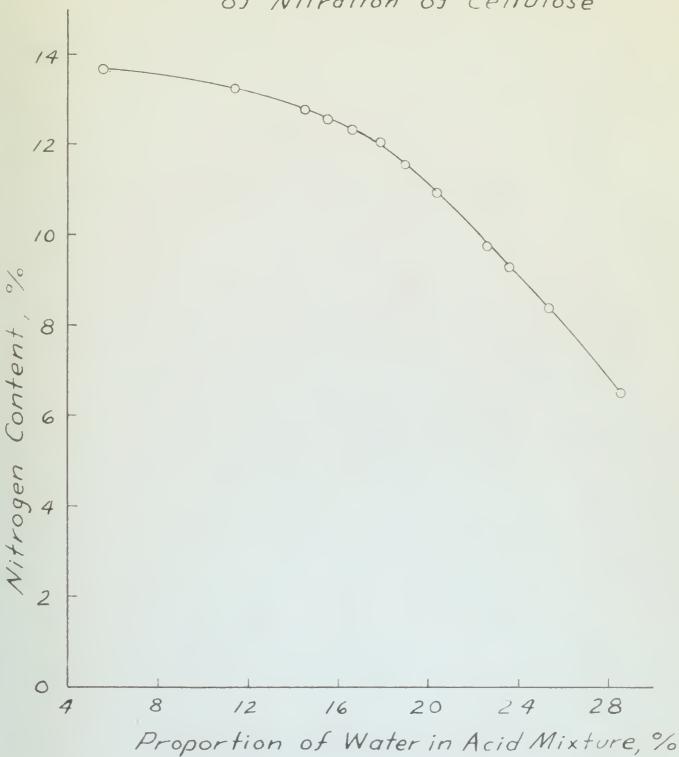
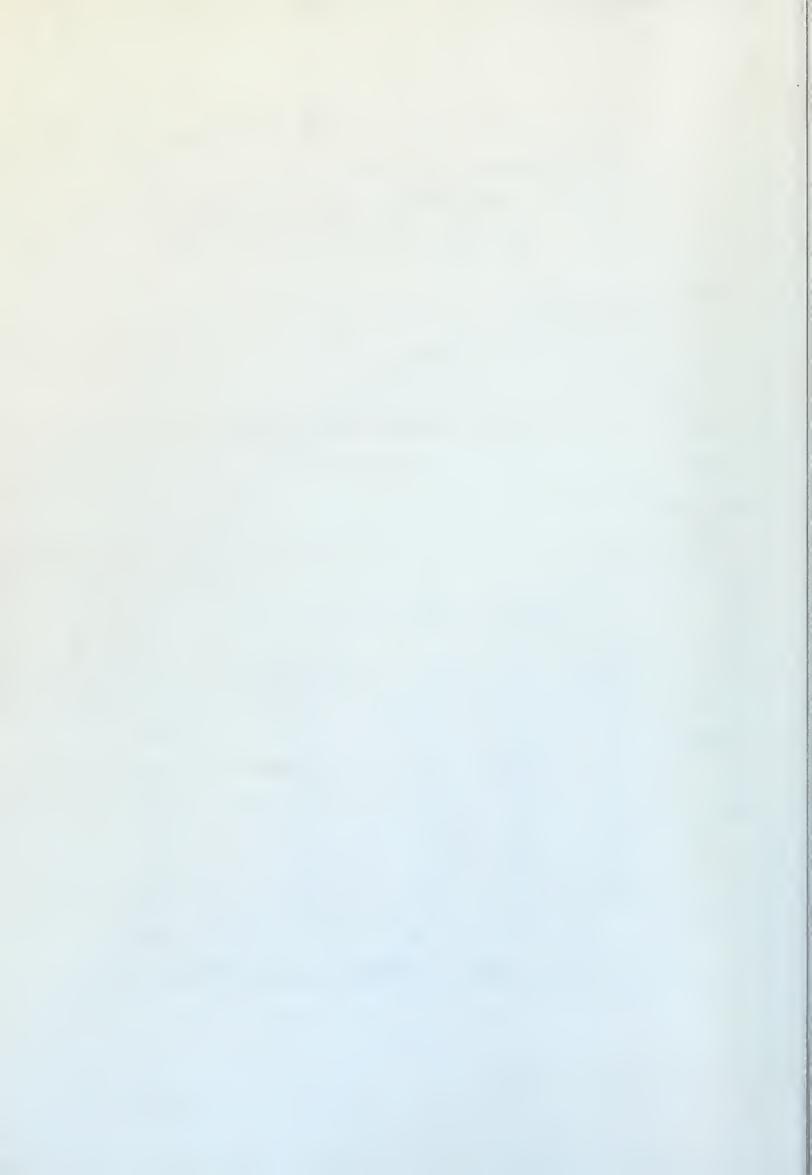


Fig. 1



content is readily seen (Fig. 1). As the mixed acid becomes more dilute, the degree of substitution decreases slowly up to a water content of about 16 per cent and more rapidly thereafter.

The results of this work by lunge and Bebie have been corroborated, in general, by several more recent investigators, including W. von Böltenstern²⁵, P. Demougin²⁵, and Shiemann and Kühne¹⁶.

The latter two investigators observed that, if the water content in the mixed acid is reduced below a certain minimum value, the nitrogen content in the resulting product is lowered. They found that a nitration mixture containing 22.6 per cent nitric acid,

76.6 per cent sulfuric acid, and only 0.82 per cent water yielded a lower percentage of nitrogen in the product than when the water centent was increased to 3.7 per cent, at which point they observed a maximum degree of substitution. They also obtained more constant percentages of nitrogen for water centents from about 5.5 per cent to 13.5 per cent than did lunge and Bebie. Above 13.5 per cent water, however, their results followed those of Lunge and Debie closely.

As shown by the experiments of behiemann and Fühne 16, there is a lower limit for the water content in the acid mixture for optimum nitration. If the mixed acid contains insufficient water, the cellulose is not completely nitrated. The resulting nitrocellulose is incompletely soluble in acetone, fine unnitrated fibers remaining undissolved. Schiemann and Kühne 16 explain this phenomenon by assuming that the extensive swelling of the fiber surfaces caused by the concentrated mixed acids prevents the penetration of the acid

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into the deeper layers of the fiber. According to bmil hueser 16, a more plausible explanation is that a certain minimum water content is necessary to cause that degree of swelling which is required to enable the mixed acid to penetrate into the interior of the micellar system.

Above 13.5 per cent water, the rate of fall in nitrogen content increases steadily up to about 20 per cent water. At this point the rate of fall becomes almost constant, but continues to change more slowly. The rate of change in this region, computed from the data of Lunge and Bebie, is about 0.6 per cent drop in nitrogen content of the nitrocellulose for each increment of one per cent of water in the mixed acid. The nitrogen content at 25 per cent water is only about 8.3 per cent. As the mixed acid reaches this degree of dilution, it exerts a considerable hydrolysing effect upon the cellulose. The detrimental effect of this hydrolyzing action is manifest in the increasing brittleness and harshness of the nitrocellulose produced. Moreover, at these high water contents the cellulose dissolves in the acid to a considerable extent.

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THE INFLUENCE OF SULFURIC ACID IN THE NITRATION ACID

The Effect of the Mixed Acid Composition Upon the Attainment of Maximum Nitration

The influence of sulfuric acid upon the extent of nitration of cellulose was investigated by P. Vielle as early as 1883. He observed that the degree of substitution is increased by the addition of sulfuric acid te dilute nitric acid. Lunge and soworkers with the acid upon the degree and rate of substitution. In their first group of experiments, they attempted to get a product with the theoretical 14.14 per cent nitrogen content, using various mixed acid and water compositions. Their products, as shown below, ranged from 13.51 per cent to 13.92 per cent nitrogen content.

Effect of Mixed Acid Composition on the Attainment of Maximum Mitration of Cellulose 18

No.	H2504,	ion of Mix HNO3, Per Cent	Nitrogen in Nitrocellulose Per Cent		
1	60.00	27.43	12,57	13.62	
2	62.10	25.79	12.11	13.78	
3	62.95	24.95	12.10	13.83	
4	63.72	25.31	10.97	13.75	
8	64.56	24.65	10.79	13.71	
6	68.02	25.28	5.70	13.78	
7	64.65	26.85	8.88	13.72	
8	63.35	25.31	11.34	13.92	
9	75.33	22.80	1.87	13.53	
10	74.16	22.12	3.72	13.51	
11	72,97	21.63	5.40	13.57	
12	69.90	20.45	9.66	13.64	
13	68.31	20.49	11.20	13.61	
14	67.43	19.37	13.20	13.25	
15	67.32	32.53	0.15	13.62	
16	65.41	31.34	3.26	13.57	
17	63.75	30.80	5.45	13.63	
18	70.88	29.31	10.01	13.68	

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The Effect of Varying the Proportion of Sulfuric Acid to Nitric Acid

Lunge and Meintraub¹⁸ studied the effect of varying the propor
tion of sulfuric acid to nitric acid upon the degree and rate of

nitration. They nitrated two and one-half graze of cotton with

thirty grams of nitric acid (density 1.52) and varying quantities of

sulfuric acid at a temperature of about 19° to 20°C. Their data are:

Influence of Varying the Proportion of Sulfurie Acid to Nitric Acid18

Parts H ₂ SO ₄ to 1 part HNO ₂	After one-ha Nitrogen in Nitrocallulose, Fer Cent	Yield, Per Cent	Nit	ter twenty-fo itrogen in recellulose, Per Cent	Yield, Per Cent
0	12.58	162.75		12.62	163.32
0.1	40	top		12.66	165.02
0.25	13.45	175.69		13.44	175.77
0.50	6400	•		13.42	175.22
1.0	13.36	174.56		13.39	174.75
2.0	13,23	174.14		13.32	175.98
3.0	12.72	166.14		13.40	176.44
4.0		640		13.20	175.12
5.0	8.14	130.88		13.10	166.60
	After three	days	4	After fifteen	daya
6.0	12.63	162.40		12.74	169.80
7.0	10.66	151.60		900	***
	After eight	days		After thirty	days
8.0	10.88	144.62		11.70	152.0
9.0	7.74	120.11			
10.0	5.43	65.0			

As the ratio of sulfuric acid to nitric acid is increased, the rate of nitration drops rapidly. With less than one part of sulfuric acid to one part of nitric acid, the final stage of nitration is reached in one-half hour. With the acids in the ratio of three to one, at the end of the first half hour the nitrogen content is

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12.72 per cent, the final content being 13.40 per cent. Then a ratio of eight parts sulfuric acid to one part nitric acid is used, the final stage of nitration is not reached after eight days, and only after thirty days is it equal to 11.70 per cent nitrogen.

The maximum nitration is obtained with ratios of sulfuric acid to nitric acid between one-fourth to one and three to one. With ratios above eight to one, the product always contains some unchanged cellulose. The excess sulfuric acid also affects the fiber structure. Instead of retaining its original structure on drying, it falls into a finely fibrous powder.

The affect of Varying the proportion of Sulfurie Acid, aintaining a Constant natio of Aitric Acid to mater

Lungo and Bebie¹⁸ nitrated cellulose, maintaining the proportion of nitric acid to that of water constant and varying the quantity of sulfuric acid. Twenty-five parts by weight of nitric acid and fourteen parts water to one part of cotton were used. The data are:

of Fitric Acid to Later and Variable quantities of Sulfuric Acid

No.	Composit H2SO4, Per Cent	ion of lix HNO3, Per Cent	H ₂ O,	Fitrogen in Nitrocellulose, Per Cent	Yield,
1	38.47	40.19	21.34	10.32	142
2	40.83	38.72	20.45	10.76	151
3	42.92	37.40	19.68	11.02	153
4	48.03	34.18	17.79	12.23	155
5	49.37	33.38	17.25	12.77	166
6	50.71	32.50	16.79	13.02	165
7	52.81	31.27	18.98	13.11	147
8	54.92	30.06	15.02	13.48	173

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Lunge and Bebie concluded that the presence of sulfuric acid favors, or, by way of activation, furthers the introduction of nitrate groups into the collulese molecule when nitrating collulese with a sulfuric acid, nitric acid and water mixture.

Cross, Bevin, and Jenks⁵, and Robertson²⁶ suggest that the sulfuric acid participates in the process of esterification, and that sulfuric acid esters form first and the sulfuric acid radicals of the cellulose are replaced by nitrate groups. During the first few moments of nitration with mixed acids, the sulfuric-acid content of the product is rather high, but it drops rapidly as nitration proceeds. It has been found by analysis 11 that some sulfuric acid is still present in the ester form in the final product. This combined sulfuric acid is extremely objectionable, since it tends to cause subsequent decomposition of the nitrocellulose.

The Effect of Sulfuric Acid Upon the Nitric Acid Vapor Pressure, and its Pelation to the Nitrating Capacity of the bixed Acid

The influence of sulfuric acid upon the nitrating capacity of mixed acid was further investigated by Saposehnikow²⁷ who observed a relationship between the nitric acid vapor pressure of various mixed acid concentrations and the nitrogen content of the nitrocellulose produced by them. He noted the change in vapor pressure and concentration of nitric acid as sulfuric acid was added. Unon adding the sulfuric acid, the vapor pressure of the nitric acid rose until a certain concentration was reached. Then it diminished as more sulfuric acid was supplied. Saposehnikow observed that the mixed acid concentration which exerted a maximum nitric acid vapor

APPROXICATION OF THE RESIDENCE AND ADDRESS OF THE PARTY ADDRESS OF THE PARTY AND ADDRESS OF THE PARTY ADDRESS OF THE PA

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pressure was approximately the same concentration which produced nitrocallulose with the highest nitrogen content.

According to Saposchnikow, as the sulfuric acid is added initially, it deprives the nitric acid, which is present in the form of its hydrate, of its water content and forms hydrates of varying composition. As the water is taken up by the sulfuric acid, the concentration of free nitric acid increases and, consequently, its vapor pressure rises. The maximum vapor pressure is exerted when just enough sulfuric acid has been added to cause all of the nitric acid to exist as PIO_2 . Further addition of sulfuric acid results in the gradual dehydration of the nitric acid to the anhydride, E_2O_5 , which has a very small vapor pressure. As the dehydration of the nitric acid to the anhydride proceeds, the effectiveness of the acid mixture as a nitrating agent diminishes.

Upon the addition of water, the above transitions proceed in the reverse order; the excess water reduces the effect of the sulfuric acid so that the nitric acid anhydride is reconverted into hill, which, in turn, is reconverted into its hydrate.

Berl and Saenger³ have confirmed capeschnikow's results, but they suggest that nitric anhydride forms an addition compound with nitric acid, N₂O₅(NNO₃)₆. They believe that this addition compound, rather than the anhydride itself, is responsible for the lowering of the nitric acid vapor pressure and, hence, in the concentration of the free nitric acid when the amount of sulfuric acid is increased beyond a point corresponding to the maximum nitric acid vapor pressure. The existence of sulfuric acid in the form of its

 monchydrate, H2504 ·H20, when the nitric acid vapor pressure reaches its maximum value, has been confirmed by measurements of the heat of reaction evolved from nitric acid, sulfuric acid and water systems.

The relationship between the vapor pressure exerted by the mixed acid and the nitrogen content of the nitrocellulese produced is shown in the accompanying graph (Fig. 2). According to Sapeschnikew, maximum nitration occurs when all of the nitric acid exists as RNO3 and the minimum degree of substitution results when all of the nitric acid exists as the hydrate, HNO3°H2O, corresponding to the maximum and minimum nitric acid vapor pressures, respectively. On the basis of his experiments, Saposchnikow concluded that the most suitable mixture for yielding the maximum degree of nitration should have the following composition:

24.29% HNO3 65.80% H23C4 9.91% H20

This does not differ appreciably from the mixed acid composition used by Lunge and Bebie (page 12) in obtaining their maximum degree of nitration of 13.92 per cent nitrogen.

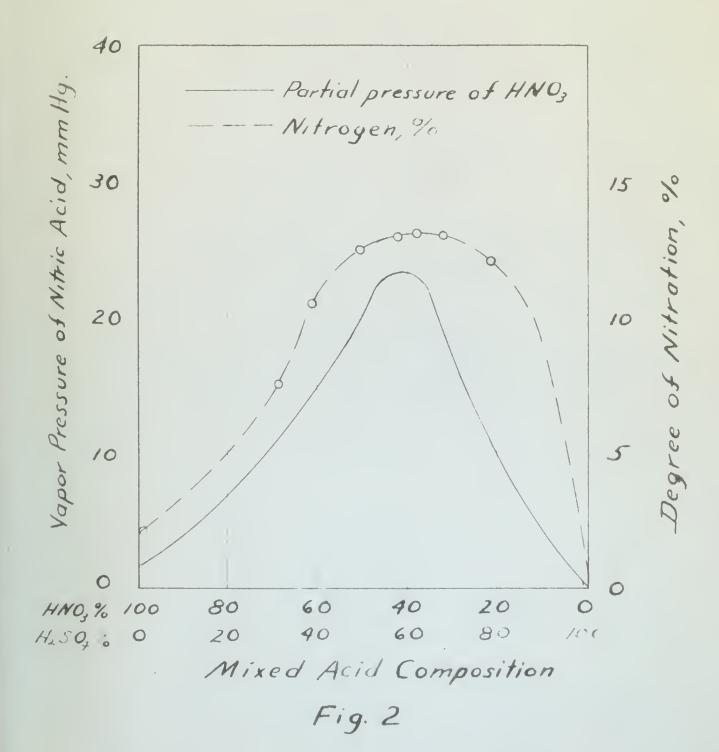
The Correlation of the Extent of Witration and the Spent Acid Composition

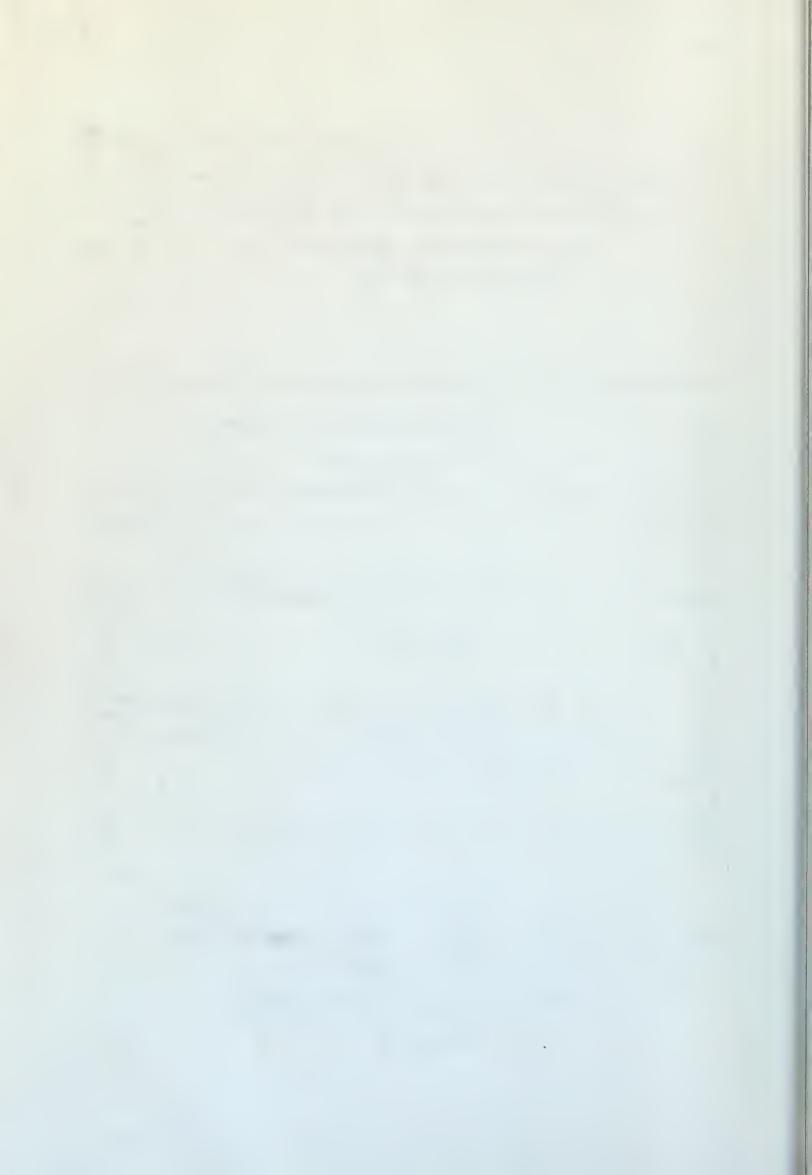
the nitrogen content of mitrocellulose with the compositions of spent mitrating acids (Fig. 3). They contend that mitration is an equilibrium reaction and that the final mitrogen content depends upon the composition of the spent acid in contact with the mitro-

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The Relationship between Nitrogen Content of Nitrocellulose and Vapor Pressure with increasing Amounts of Sulfuric Acid





The Effect of Spent Acid Composition on the Nitrogen Content of Nitrocellulose

Lines of Equal Nitration Degree (%N)

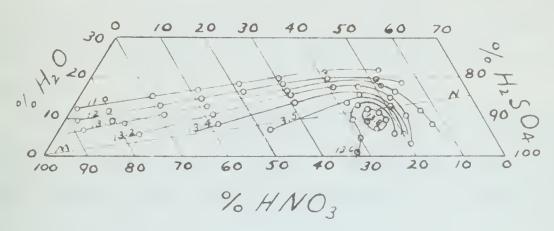


Fig. 3



cellulose, rather than upon the initial mixed acid composition.

Armst Berl and coworkers 25 also confirmed and extended sapeschmikow's work. On the triangular diagram correlating the nitrogen content of nitrocellulose and spent acid composition, the broken line "NN" joins the points corresponding to compositions which exert maximum nitric acid vapor pressures. Berl and coworkers point out that on approaching this line the nitrogen content increases with a decrease in water content, and that the maximum nitration is attained with a spent acid whose composition lies on this line. This composition corresponds to:

This is equivalent to a ratio of 1 HNO3 to 2 (H2SO4. H2O), representing the case in which all of the water is combined with the sulfurio acid and all of the mitric acid is available for nitration.

arnst Berl and coworkers 16 have critically analyzed the nitration data of a great number of previous investigators and found excellent confirmation of Saposchnikow's and their own work.

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THE I.FLU. ACE OF THE KATLO OF TAKE ACID TO CILLULOUS

A certain minimum quantity of mixed acid is required to penetrate and nitrate a given quantity of cellulose uniformly. The physical structure of the cellulose has some effect upon the ease with which it is penetrated by the acid, hence, it affects somewhat the choice of the ratio of acid to cellulose. For example, paper is penetrated more easily than loose cotton, which tends to lump together and thus to impede uniform diffusion of the acid 12.

Although ectton is the purest form in which celluless occurs in nature and has been the chief source of cellulose for the manufacture of nitrocellulose, other cellulosic materials have been used 24. A mixture of equal parts of wood pulp and cotton linters 31, or wood pulp alone, when properly prepared and purified 28, are suitable for nitration.

For each molecule of nitric acid entering the cellulose chain, one molecule of water of reaction is produced. Unless this water is removed, it dilutes the nitric acid and decreases its power of nitration. If the ratio of the acid mixture to cellulose is large, the influence of the water of reaction is diminished.

twenty-five to one, the effects of non-uniform penetration and the influence of the water of reaction are still apparent. At a ratio of forty to one, these effects diminish appreciably, and they practically disappear at ratios from fifty to one to eighty to one.

A ratio of forty parts mixed acid to one part cellulose represents

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an excess of ten to twelve times more than is theoretically required to produce nitrocellulose with a nitrogen content of 11.0 to 11.5 per cent.

Lunge and Sebie¹⁸, using a ratio of mixed acid to cellulose of twelve to one, found that by raising the ratio of sulfuric acid to nitrio acid from one to one to a ratio of three to one, the nitrogen content is increased 0.3 per cent. Under similar cenditions, but using a mixed acid to cellulose ratio of thirty to one, the rise in nitrogen content is 0.63 per cent. This represents a difference of 0.33 per cent increase in nitrogen centent caused by the larger ratio of mixed acid to cellulose.

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THE INFLUENCE OF TEMPERATURE, TIME, AND AGITATION

The Effect of Temperature and Reaction Time Upon the Degree of Substitution

both the reaction rate and the degree of substitution. As in the case of most chemical reactions, a rise in temperature tends to increase the reaction rate and the extent of nitration, up to a certain point. Lungs and coworkers have investigated the relationship between the temperature, the duration of the reaction, and the degree of substitution. Their results are:

Effect of Temperature and Reaction Time on the Nitration of Cellulese 18

Temperature,	Time,	Witrogen in Witrocellulose, Per Cent	Yield (Actual), Per Cent	Yield(Cal- culated), Per Cent
0	0.5	10.71	162.3	183
0	7	13.19	173.3	174
10	7	13.37	175.8	176
15	7	15.38	175.6	176
19	0.5	12.72	166.1	170
19	7	13.39	175.6	176
40	0.5	13.07	172.3	173
40	7	13.06	169.6	173
60	0.5	13.08	169,2	178
60	4.5	13.07	162.1	173
80	0.25	13.07	161.2	173
80	0.8	13.12	128.2	173
80	3	13.12	81.5	173

The nitrations were effected with a three-to-one mixture of sulfuric acid and nitric acid. The yields were based on the weight of cellulose employed; that is, the percentage yield is the weight of nitrocellulose obtained from one hundred parts of cellulose.

The velocity of the reaction increases rapidly with a rise in

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of seven hours, while at 40°C., the nitrogen content reaches its highest value at the end of one-half hour and, at 80°C., it is nearly at a maximum value at the end of fifteen minutes. The nitrogen content of the product drops a little when the temperature of the reaction is raised from 19°C. to 40°C., but it remains about the same as the nitration temperature is further increased.

The use of reaction temperatures higher than 40°C., while having a favorable effect upon the velocity of the mitration, results in a smaller yield of mitrocellulose. At high temperatures, the acid mixture not only esterifies but also exerts oxidising and hydrolyzing effects upon cellulose. These side reactions, in addition to lowering the yield of mitrocellulose, give rise to undesirable degradation products. Lunge and Bebie¹⁸ also observed that mitration at a higher temperature causes a change in the structure of cellulose. As the temperature of mitration is increased, the fibers become shorter and more fragile and, at 60° to 80°C., a finely fibrous powder is obtained.

Lunge and Bebie¹⁸ pointed out that if the proportion of sulfuric acid to nitric acid is greater than three to one, the drop
in yield on raising the reaction temperature is even more strongly
pronounced. With a ratio of eleven to one, an increase of a few
degrees in the reaction temperature has the same effect as a
twenty-or thirty-degree increment with an acid in the proportion
of three to one.

For each reaction temperature there is a corresponding optimum

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time of reaction. At ordinary temperatures, the margin is rather wide, but at higher temperatures, the nitrogen content rises at first and, upon longer action, decreases again. Thus, at a temperature of 32°C., using an acid mixture containing three parts sulfurie acid to one part nitric acid, lunge and Bebie¹⁸ measured the following nitrogen contents after the time intervals indicated:

Time of Reaction, Ninutes	Mitrogen Content of Witrocellulose, Per Cent
5	13.27
15	13.44
30	13.47
60	13.50
120	13.40

In this case, the optimum time of reaction is one hour.

The Rate of Mitration of Ramie

The rate of substitution for bleached and umbleached ramie was determined by Sakurada¹⁶. He performed the nitrations with an acid mixture of one volume of nitric acid (density 1.52) to two volumes of sulfuric acid (density 1.84) at a temperature of 0°C.

Rate of Mitration of Bleached and Unbleached Ramie Fiber 16

Bleached Ramie			Unbleached Ramie				
Time,	Ritrogen Per Cent	Fitrate Groups Per Unit Composit	Time, Sec.	Nitrogen Per Cont	Nitrate Groups Per Unit Celloos		
60	40	••	15	1.53	0.20		
45	3.18	0.42	48	2,11	0.27		
90	3.91	0.52	90	2.71	0.35		
300	5.63	0.78	300	4.55	0.61		
600	7.67	1.16	599	€.86	0.82		
1,800	11.07	2.00	1,800	9.05	1.49		
8,600	12.68	2.48	5,600	11.82	2.20		
18,000	13.85	2.89	18,000	13.80	2.87		

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The initial rate of substitution of nitrate groups in the collulose molecule was rather rapid. With bleached ramie, the nitrogen content at the end of forty-five seconds was 5.18 per cent; after ten minutes, it rose to 7.67 per cent. As the reaction continued, however, the rate of substitution dropped; the maximum degree of substitution was not reached until after five hours.

The Rate of Mitration of Cotton Linters and Wood Pulp

Schiemann and Kühne¹⁶ investigated rates of nitration of cotton linters and wood pulp. For cotton linters a mixed acid composition of 42.58 per cent nitric acid, 53.72 per cent sulfuric acid, and 3.72 per cent water was used; for the wood pulp, the composition of the mixed acid was 43.58 per cent nitric acid, 53.41 per cent sulfuric acid, and 3.21 per cent water. A collulose to mixed acid ratio of one to eighty was used and the temperature of reaction in the case of cotton linters was 17°C, and for wood pulp 15°C.

Rate of Mitration of Cotton Linters and Wood Pulp16

Tipe of Bitration	Nitrogen Con- Cotton Linter	tent, Per Cent s Wood Pulp
1.0 minutes	12.21	905
5.5	13.24	12.47
10.5	13.49	13.39
15.0	gica	13.39
15.5	13.58	13.62
30.0 tt	un .	13.59
32.0 *	13.62	**
1.0 hours	13.61	13.61
2.0 "	13.58	13.62
3.0 "	13.62	**
4.0	13.59	13.61
5.0 #	13.61	
6.0 ¹¹	100	13.62

With cotton linters, substitution to 12.21 per cent nitrogen

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was reached after only one minute. Almost the maximum degree of nitration was attained after five and one-half minutes in the case of the cotton linters and after ten and one-half minutes in the ease of the wood pulp.

Although the results of Shiemann and Kühne are not quite comparable to those obtained by Sakurada with ramie, the more rapid rate of nitration of the cotton linters and wood pulp was probably due primarily to the higher temperature employed.

The Effect of Agitation

Agitation tends to increase the rate and uniformity of nitration. Agitation has the effect of rendering all of the surface of the cellulose accessible to the acid mixture so that penetration and reaction can proceed quickly and uniformly. J. O. Small and C. A. Higgins 30 state that, under identical conditions, there is a difference of nearly 0.2 per cent in nitrogen centent between material that is thoroughly agitated during nitration and material that receives no agitation.

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THE MAXIBUM DEGREE OF NITHATION OF CALLULOSE ATTAINED

Factors Limiting the Degree of Mitration with Wixed Acid

Nitrocellulose containing 14.14 per cent nitrogen, corresponding to cellulose trinitrate, has never been prepared by nitrating cellulose with a mixture of sulfuric acid and nitric acid. The nearest approach to this theoretical maximum value was reported by C. E. Hake and E. Bell¹⁰, who prepared nitrocellulose containing 15.96 per cent nitrogen with a mixed-acid ratio of three parts sulfuric acid to one part nitric acid.

The failure to attain the theoretical degree of substitution corresponding to the trinitrate has been attributed to the reversibility of the nitration reaction and to the tendency of sulfuric acid to enter into the reaction to form esters in competition with the nitric acid. The existence of equilibria has been demonstrated by Berl and coworkers^{2,16}, who showed that equilibrium can be approached from either direction and that the nitrogen centent of mitrocellulose is determined by the final acid composition in contact with the nitrocellulose.

acid in the nitrating mixture participates in the esterification, with the resulting formation of a mixture of sulfuric and nitrie esters⁵.10,26. R. Robertson²⁶ suggested that the formation of sulfuric acid esters occurs first and that, subsequently, the replacement of the sulphate radicals by nitrate groups takes place.

Another explanation for the failure to reach complete nitration with mixed acid has been proposed by R. C. Farmer 9. He suggested

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that the esteristication with nitric acid occurs most readily through its "pseudo" form, O2E.OH, and explained that, in the mixed acid concentration required for the maximum nitration of cellulose, the nitrating action is hindered by the formation of nitronium sulfate, (10)3 (804B)2, and that this partial removal of the pseudo nitric acid prevents the formation of cellulose trinitrate.

Laximum Degree of Vitration Attained by Various Investigators

Numerous other nitrating agents have been used for the nitration of collulose, but none have approached the commercial importance of the sulfurio acid, nitric acid, and water mixture. Collulose trinitrate, containing 14.14 per cent nitrogen, has been prepared by the use of a mixture of nitric acid, acetic acid, and acetic anhydride⁴. The highest nitrogen contents obtained by various investigators and the compositions of the nitrating agents employed are:

Maximum Degree of Mitration of Cellulose Attained by Various Investigators 14

Investigator	Composition of Nitrating Agent	Tempera- ture C.	Time, Hours	Per Cent Nitrogen Cotained
J. 1. Bar	3 vol. HDO2 (d 1.5) 1 vol. H2304 (d 1.845)	10	24	15.74-13.91
P. Vielle	HNO3 (d 1.502)	11	***	13.4
L.Vignon	38805 (d 1.6):182804 (d 1.84)	~. Š	24	15.5
O. Guttermann	lot given	•	-	13.66
O.Lure in L. Weintraub	18003:17203	16-20	24	15.07

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d/d	10			
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Levesticstor	Composition of Nitrating Agent	Tempera-	Time,	
G.Lunge and J. Bebie	26.31% HFO3, 65.35% H ₂ SO ₄ , 11.34% H ₂ O	18-20	24	13.92
C.Hoitsema	N205 and HNO3	18-20	48	14.0
E. Berl and R.	E205	Der		13.86
F. Sake and M.	1Ha03:3H2604	99		13.96
E.Berl and ". Smith, Jr.	lumOz (d 1.48) : 3 Acetic anhydride : 1 Acetic acid	18-20	48	13.70
R. Delmon, J. Cheon lin, L. Frissaud	F ₂ O ₅ disselved in		6	14.0
E.Dalmen ⁶	NgOs in current of oxygen	ste.	•	14.12
L.Louchonnot, F. Prombe, and C.F. itpus	Kitrio acid vapor	~	400	25.0
A. Jeuchennet, F. Trombe, and G. Petitpas ⁴	50% ENG, 25% Acetic Anhydride, 26% Acetic Acid	15	8	14.14

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SUDBARY

Nitrocellulose of various degrees of substitution can be prepared by the esterification of cellulose with a mixture of sulfuric acid, nitric acid, and water. There is evidence that the reaction approaches equilibrium over a wide range of substitution. The composition of the product and the reaction rate depend upon the conditions of the nitration, which include, the composition of the mixed acid, the ratio of mixed acid to cellulose, the temperature of the reaction, the duration of the reaction, and the agitation employed.

The effect of the propertion of water in the nitration acid is very pronounced. Insufficient water results in incomplete nitration of the cellulese. On the other hand, if the water centent exceeds about 13.5 per cent, the degree of substitution drops rapidly. The primary function of sulfuric acid in the nitration mixture is that of dehydration. Since it has a greater affinity for water than nitric acid, it forms hydrates, leaving the nitric acid free to react with the cellulose. A ratio of sulfuric acid to nitric acid between one-fourth to one and three to one produces the highest degree of substitution. The theoretical optimum molar ratio of nitric acid, sulfuric acid, and water in spent acid in contact with the resulting nitrocellulose is 1HNO3:2H2SO4:2H2O.

A high ratio of mixed acid to cellulose is conducive to a high degree of substitution. The influence of a large excess of nitrating acid is twofold; it serves to minimize the diluent effect of water produced by the reaction and it promotes more rapid and more uniform

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penetration of the cellulese by the scid.

The temperature, time of reaction, and agitation employed are semewhat interdependent. Agitation and a rise in temperature increase the velocity of reaction and the degree of substitution up to a certain point. Above 40°C., although the reaction rate continues to rise, the extent of nitration does not increase as the temperature is further increased, and the yield becomes less. In addition, high temperatures promote the oxidation and hydrolysis of the cellulose by the acid, thereby lowering the yield and giving rise to undesirable degradation products.

Nitrocellulose containing the theoretical maximum nitrogen content has never been prepared with a mixture of nitric acid and sulfuric acid. The reversibility of the reaction and the esterification action of the sulfuric acid account for the failure to attain the trinitrate.

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EIELIOGRAPHY

- 1. Adams, N. R., Trans. Faraday Sco., 29, 95 (1933).
- 2. Berl, E. and E. Berkenfield, Z. angew. Chem., 54, 1056 (1929).
- 5. Berl, E. and H. E. Saenger, Monatch, 63 and 64, 1036 (1929).
- 4. Bouchonnet, A., F. Trombe, and G. Petitpos, Compt. rend., 197, 63 (1933).
- 5. Cross, C. F., E. J. Bevin, and R. L. Jenks, Ber., 34, 2496 (1901).
- 6. Dalmon, R., Compt. rend., 201, 1123 (1935).
- 7. Dalmon, R., J. Checlin, and L. Brissaud, Compt. rend., 201, 664 (1935).
- 8. Davis, Tenney L., "The Chemistry of Fowder and Emplosives", p. 244, 251, John Wiley & Sons, Inc. (1943).
- 9. Farmer, R. C., J. Soc. Chem. Ind., 50, 75T (1931).
- 10. Hake, C. N. and M. Bell, J. Soc. Chem. Ind., 28, 461 (1909).
- 11. Hake, C. E. and R. J. Lewis, J. Sec. Chem. Ind., 24, 374-81 (1905).
- 12. Guttermann, O., J. Soc. Chem. Ind., 28, 461 (1909).
- 13. Merseg, R. O. and St. von Warsy-Szabo, Z. physik. Chem., 134, 264 (1928).
- 14. Hess, Kurt, "Die Chemie der Zellulose und Ihrer Begleiter", p. 364, Akademische Verlagegesellschaft M.B.H. Leipzig (1928).
- 16. Hess, Kurt, and C. Tregus, Z. physik, Chem., B15, 157 (1931).
- 16. Heuser, Emil, "The Chemistry of Cellulose" p. 172-189, John Wiley & Sons, Inc. (1944).
- 17. Lorand, R. J. and E. A. Georgi, J. Am. Chem. Soc., 59, 1166 (1937).
- 18. Lunge, G., J. Am. Chem. Soc., 23, 527 (1901).
- 19. Mark, H., "Physik und Chemie der Cellulose", p. 267, Julius Springer (1952).

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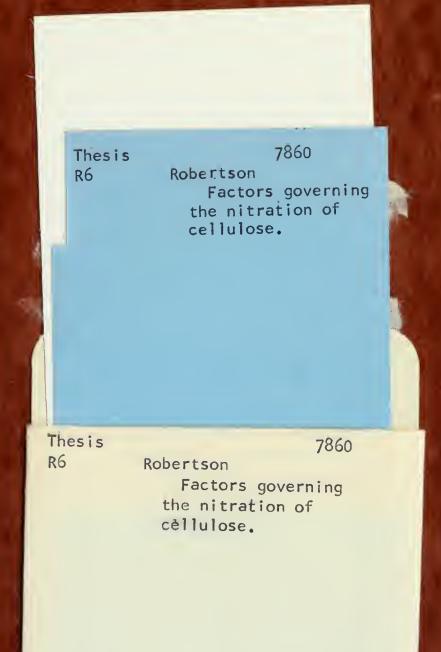
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- 20. lathiou, M., "rans. Faraday Soc., 25, 122 (1933).
- 21. Miles, F. D. and J. Craik, J. Phys. Chem., 34, 2607 (1930).
- 22. Liles, F. P. and L. Lilbourn, J. rhys. Chem., 34, 2598 (1930).
- 23. laray-Szabo, St. v. and G. von Susieh, Z. physik, Chem., 134, 264 (1928).
- 24. Olsen, F., Ind. Eng. Chem., 21, 354 (1929).
- 25. Ott, Smil, "High Polymers", Vol. 5, p. 622-540, Interscience Publishers, Inc. (1945).
- 26. Rebertson, R., J. Sec. Chem. Industry, 25, 624 (1906).
- 27. Saposchnikow, A., Z. physik. Chem., 49, 697 (1904); 51, 509 (1905); 53, 225 (1905).
- 28. Shur, M. O. and F. G. doos, Ind. Lng. Chem., 29, 26 (1937).
- 29. Sissen, M. A., Ind. Eng. Chem., 30, 530 (1938).
- 30. Small, J. O. and C. A. Higgins, Chemical Age, 28, 215 (1920).
- 31. loodbridge, R. G., J. Ind. Png. Chem., 12, 38 (1920).
- 32. Forden, E. C., "Technology of Cellulose Esters", Vol. 1, part 3, p. 1567, Eschen bach Frinting Co. (1921).

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